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Nitrogen-15 Magnetic Resonance Spectroscopy. V. Oxygen-Nitrogen Compounds.

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Nitrogen-15 Magnetic Resonance Spectroscopy. V. Oxygen-Nitrogen Compounds.[1]

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The ^{15}N chemical shifts of a series of oxygen-nitrogen compounds have been found to vary over a range of 576 p.p.m. Since the calculated range of the diamagnetic contribution is only 80 p.p.m., the paramagnetic term must dominate. An observed correlation between the ^{15}N chemical shifts and the energy of the $\underline{n} \rightarrow \pi^*$ transitions substantiates this interpretation

experimentally. For compounds such as nitric acid, which lack nonbonding electrons on nitrogen, contributions to the mean electronic excitation energy from nonbonding oxygen electrons may be important.

Magnetic shielding of nitrogen nuclei has in general been attributed to the paramagnetic term,[3-7] which arises from changes induced

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(3) B. E. Holder and M. P. Klein, J. Chem. Phys., 23, 1956 (1955).

(4) B. M. Schmidt, L. C. Brown, and D. Williams, J. Molecular Spec., 2, 539, 551 (1958); ibid., 3, 30 (1959).

(5) J. B. Lambert, G. Binsch, and J. D. Roberts, Proc. Natl. Acad. Sci, US, 51, 735 (1964).

(6) D. Herbison-Evans and R. E. Richards, Mol. Phys., 8, 19 (1964).

(7) J. B. Lambert, Ph. D. Dissertation, California Institute of Technology, 1965, pp. 69f.

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by the external field in the electronic wave functions, as represented by mixing of the ground state with excited states. This assumption has received some experimental confirmation by correlations of the chemical shift with the energy of transitions involving low-lying excited states, in particular the $n \rightarrow \pi^*$ transition,[5-9] which would dominate the so-

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(8) J. D. Baldeschwieler and E. W. Randall, Proc. Chem. Soc., 1961, 303.

(9) V. M. S. Gil and J. N. Murrell, Trans. Faraday Soc., 60, 248 (1964).

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called mean electronic excitation energy, ΔE. We have approached the problem of nitrogen chemical shifts in oxygen–nitrogen compounds from an entirely empirical point of view, through comparison of the chemical shifts with the corresponding electronic spectra. Consideration of compounds in which oxygen is bonded directly to nitrogen is complicated by the possibility of contributions to the mean electronic excitation energy from orbitals on oxygen.

Following a method developed by Professor S. I. Chan,[10] we

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(10) We are indebted to Professor Chan for describing the computational techniques to us prior to their publication. Most of the bond lengths used in these calculations are those listed in A. F. Wells, "Structural Inorganic Chemistry," Oxford University Press, London, 1962, pp. 616 f. See S. I. Chan, M. R. Baker, and N. F. Ramsey, Phys. Rev., 136, A1224 (1964); and S. I. Chan and A. S. Dubin, J. Chem. Phys. (to be published).

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have calculated the diamagnetic contributions (σ^D) to the shieldings[11]

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(11) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Company, Inc., New York, 1959, pp. 165 f.

(Table I). Only the effects of directly bonded atoms have been taken into consideration. These calculations assume that σ^D for the nitrogen atom is 325 p.p.m.[11,12] The accuracy of this number, however, has

(12) W. C. Dickinson, Phys. Rev., 80, 563 (1950).

no bearing on the differences between the values of σ^D in Table I, since in each case, σ^D of the nitrogen atom enters only as an additive constant. On this same scale, σ^D for the ammonium ion (chemical shift = 24 p.p.m.) is 360 p.p.m. Thus, there are differences of 70 to 150 p.p.m. between σ^D for the ammonium ion and for the oxygen–nitrogen compounds studied here. The important point, however, is that the range of σ^D for the oxygen–nitrogen compounds is only 80 p.p.m., whereas the range of chemical shifts is 576 p.p.m. The large variations observed in this series may justifiably be attributed to changes in the paramagnetic term. We have therefore compared the chemical shifts of the oxygen–nitrogen compounds listed in Table I with the energy corresponding to their respective lowest $n \rightarrow \pi^*$ transition.

The compounds fall into two groups, those with nonbonding electrons which are only on oxygen (s-butyl nitrate, nitrate ion, and nitrobenzene), and those with nonbonding electrons which are both on oxygen and on nitrogen (n-butyl nitrite, nitrite ion, and nitrosobenzene). s-Butyl nitrate appears to bear the same relationship to the nitrate ion as n-butyl nitrite does to the nitrite ion. In both cases the nitrogen of the ester comes at slightly higher field, and the observed ester $n \rightarrow \pi^*$

Table I. Chemical Shifts and Absorption Maxima of Oxygen-Nitrogen Compounds

	λ_{max} ($\underline{n} \rightarrow \pi^*$), mμ	σ^D, p. p. m.	Chemical shift, p. p. m.[h]
s-Butyl nitrate	270[a] ($\underline{n}_O$)	500[f, g]	337[i]
Nitrate ion	300[b] ($\underline{n}_O$)	510	367
Nitrobenzene	330[c] ($\underline{n}_O$, ?)	490	372
n-Butyl nitrite	356[d] ($\underline{n}_N$)	440	572
Nitrite ion	380[e] ($\underline{n}_N$)	450	608
	300 ($\underline{n}_O$)		
Nitrosobenzene	755[c] ($\underline{n}_N$)	430	913

[a] H. E. Ungnade and R. A. Smiley, J. Org. Chem., 21, 993 (1956).

[b] H. M. McConnell, J. Chem. Phys., 20, 700 (1952).

[c] J. N. Murrell, "The Electronic Spectra of Organic Molecules," John Wiley and Sons, Inc., New York, 1963, pp. 186 f.

[d] R. N. Haszeldine and J. Jander, J. Chem. Soc., 1954, 691

[e] W. G. Trawick and W. H. Eberhardt, J. Chem. Phys., 22, 1462 (1954).

[f] See footnote 11.

[g] Absolute shielding, referred to the nitrogen nucleus.

[h] Downfield from external anhydrous ammonia.

[i] M. Witanowski, private communication on nitrogen-14 data.

transition is at a slightly lower wavelength. Although the changes are small, and this exact correlation may be fortuitous, one is tempted to extend the analogy to nitrobenzene and nitrosobenzene. In both cases the alkoxy group of the ester is simply replaced by a phenyl group. The structural analogy, however, does not carry over to either the absorption or the magnetic resonance spectra. Whereas the nitro compound and the nitrates all have $\underline{n}_O \rightarrow \pi^*$ transitions near 300 mμ, there is a difference of 400 mμ between the absorptions of the nitrites and the nitroso compound. This arises because the nonbonding orbital, which is located on the nitrogen atom for the nitroso-nitrite series, is strongly influenced by N-substituents.[13] For the nitro-nitrate series on the

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(13) For a discussion of this effect, see reference c in Table I.

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other hand, the nonbonding orbitals involved in the transitions of interest are those on oxygen, and hence are less affected by N-substituents. Because of the similarity of the energies of the $\underline{n}_O \rightarrow \pi^*$ transitions in the latter series, the resonance position of nitrobenzene is rather close to those of the nitrates. Since the $\underline{n}_N \rightarrow \pi^*$ transition of nitrosobenzene is of much lower energy than those of the nitrites, the paramagnetic term is immensely increased, and the resonance position was found, as predicted, at a considerably lower field (913 p. p. m. downfield from ammonia). The chemical shift of nitrosobenzene was rather insensitive to dilution and changes of solvent (chloroform, 905 p. p. m.; methanol, 908 p. p. m.; ether, 913 p. p. m.), so that no information concerning the monomer-dimer equilibrium was obtained.

The foregoing discussion has attempted to correlate the chemical shift with the energy of the $\underline{n} \rightarrow \pi^*$ absorption. For the nitro-nitrate series, the transition in question is from a nonbonding orbital on oxygen to a molecular orbital, whereas in the nitroso-nitrite series there is also a nonbonding orbital on nitrogen. It is reasonable that, in the latter cases, the $\underline{n}_N \rightarrow \pi^*$ transitions contribute more effectively to the mean electronic excitation energy, $\Delta\underline{E}$, associated with the shielding of nitrogen nuclei. Thus, the nitrites have a substantially larger paramagnetic shift than the nitrates, even though the $\underline{n} \rightarrow \pi^*$ transitions ($\underline{n}_O$ or $\underline{n}_N$) occur within a range of 100 mμ. The $\underline{n}_N \rightarrow \pi^*$ transition appears to correlate with the oxygen chemical shift also, because the nitrite ion resonance occurs about 260 p.p.m. below that of the nitrate ion,[14, 15]

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(14) H. E. Weaver, B. M. Tolbert, and R. C. LaForce, J. Chem. Phys., 23, 1956 (1955).

(15) H. A. Christ, P. Diehl, Hr. Schneider, and H. Dahn, Helv. Chim. Acta, 44, 865 (1961).

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even though the $\underline{n}_O \rightarrow \pi^*$ transitions are quite similar in both cases.

These correlations between ^{15}N chemical shifts and electronic spectra offer the possibility of aiding both in the identification of ultraviolet absorption bands, and also in the preliminary location of ^{15}N resonances. The former has been used with trans-azoxybenzene,[7] and the latter has been realized in the case of nitrosobenzene.

Experimental

The procedures for the observation of nitrogen-15 resonances and preparation of several of the labeled compounds have been described previously.[5, 7, 16] All nitrogen-15 chemical shifts were measured on a

(16) G. Binsch, J. B Lambert, B. W. Roberts, and J. D. Roberts, J. Am. Chem. Soc., 86, 5564 (1964).

Varian Model V-4300B spectrometer operated at 6.08 Mc. p. s. and 14,100 gauss. Infrared spectra were recorded on the Beckman Model IR-7.

Sodium nitrite-^{15}N was obtained from Volk Radiochemical Laboratories.

n-Butyl Nitrite-^{15}N. To a 50-ml. three-necked round-bottomed flask equipped with a thermometer and a 5-ml. syringe inserted through a syringe stopper was added a solution of 2.00 g. (0.0286 mole) of sodium nitrite-^{15}N in 7.87 ml. of water. The flask was cooled to -1° with an ice-salt bath and a solution of 0.72 ml. of concentrated sulfuric acid, 1.95 g. of n-butyl alcohol (0.0263 mole), and 0.53 ml. of distilled water was added by means of the syringe below the surface of the liquid in such a way that the temperature did not rise above +1°. During the course of the addition, which took 2 hours, the flask was shaken constantly by hand. After the mixture had remained at 0° for an hour, the sodium sulfate was removed by filtration, and the layers were

separated. The organic product was washed with sodium bicarbonate: sodium chloride: water (1:12.5:50) solution and dried over magnesium sulfate. The yield of n-butyl nitrite-^{15}N was 1.106 g. (0.0106 mole, 40.3%). The infrared spectrum contained no hydroxyl absorptions. The nitrite bands at 1615 (cis) and 1660 cm.$^{-1}$ (trans) confirmed the structure.

Nitrosobenzene-^{15}N. A mixture of 2.02 g. (1.66 ml., 0.0163 mole) of nitrobenzene-^{15}N and 1 g. of ammonium-^{14}N chloride in 33 ml. of water was placed in a 100-ml. round-bottomed flask equipped with a magnetic stirrer. Zinc (2.5 g., 0.0382 mole) was added in small portions over a 5 min. period. The temperature rose to about 50°. After 20 min., the solution was filtered to remove the zinc oxide, and the precipitate was washed with 20 ml. of boiling water. The filtrate was transferred to a 250-ml. Erlenmeyer flask and cooled quickly to 0° by the addition of excess ice. Concentrated sulfuric acid (5 ml.), cooled to 0° with about 20 g. of ice, was added quickly with stirring, and a cooled solution of 1.13 g. (0.0379 mole) of sodium dichromate in 4.2 ml. of water was added at once. The solution was filtered and washed with water. The precipitate was placed in a 100-ml. round-bottomed flask with about 20 ml. of water and steam-distilled from an all-glass apparatus. The white solid which condensed in the cooled receiver was collected in a Büchner funnel, crushed, and washed carefully with water. After being dried over calcium chloride, the nitrosobenzene-^{15}N weighed 0.664 g. (0.00614 mole, 37.7%).

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The ^{15}N chemical shifts of a series of oxygen-nitrogen compounds have been found to vary over a range of 576 p.p.m. Since the calculated range of the diamagnetic contribution is only 80 p.p.m., the paramagnetic term must dominate. An observed correlation between the ^{15}N chemical shifts and the energy of the $n \rightarrow \pi^*$ transitions substantiates this interpretation experimentally. For compounds such as nitric acid, which lack nonbonding electrons on nitrogen, contributions to the mean electronic excitation from nonbonding oxygen electrons may be important.

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